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(21) International Application Number: PCT/US93/09603 (22) International Filing Date: 7 October 1993 (07.10.93) (30) Priority data: 07/958,563 8 October 1992 (08.10.92) US (71) Applicant: NALCO FUEL TECH [US/US]; 1001 Frontenac Road, Naperville, IL 60563 (US). (72) Inventors: WOLFENDEN, Luther ; 1794 Valencia Drive, Rockford, IL 61108 (US). FISHER, Bryan ; 2168 Hartwood Drive, Kennesaw, GA 30144 (US). (74) Agents: CARVIS, Thaddius, J. et al.; St. Onge, Steward, Johnston & Reens, 986 Bedford Street, Stamford, CT 06905 (US).		(81) Designated States: CA, CZ, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ASH AMMONIA STRIPPING		
(57) Abstract The present invention relates to a process for reducing the amount of ammonia affixed to a combustion fly ash, comprising combusting a fuel under conditions effective to form a combustion fly ash and collecting the ash; and exposing the ash to a flow of air at a temperature of at least about 300 °F for at least about one minute.		

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DESCRIPTION

ASH AMMONIA STRIPPING

Technical Field

5 The present invention relates to a method for liberating or stripping the affixed ammonia (NH_3) from post-combustion fly ash generated by stationary combustion sources.

10 With the advent of technologies for the reduction of nitrogen oxides (NO_x , where x is an integer, generally 1 or 2), a pollutant often found in the combustion effluents of large industrial boilers and other combustion apparatus, the presence of ammonia in the combustion effluent as a by-product of such technologies has occurred. This is largely due to the use of nitrogenous
15 compositions such as ammonia or urea to react with and reduce the NO_x levels in the effluent stream. This phenomenon, often referred to as "ammonia slip" or "ammonia breakthrough", is believed to be caused by the introduction of stoichiometric excesses of ammonia or by the
20 formation of ammonia as a by-product in the ammonia- or urea-mediated reduction of nitrogen oxides. In addition, the use of ammonia as an effluent conditioning reagent to improve the performance of an electro static precipitator can also lead to the presence of ammonia in the effluent.

25 When substantial amounts of ammonia are present in a combustion effluent, a significant amount can become

trapped in the ash generated during combustion as ammonium salts, especially ammonium sulfate, ammonium chloride, and ammonium bisulfate, as well as absorbed free ammonia. These products are generally trapped in the ash by absorption or by being reacted and affixed to the post combustion ash. In addition, a certain amount of adsorption on the ash can occur.

When the combustion ash is later wet, such as by rain water when the ash is accumulated in an unprotected environment such as a strip mine for disposal, as is commonly done, the ammonium salts may break down, resulting in ammonia evolution into the atmosphere. In addition, where the ash is being used in the formation of concrete or other like compositions, the alkaline nature of such compositions (usually provided by the addition of lime or related substances) causes ammonia to be evolved and emitted to the atmosphere. Regardless of the reason for emission of ammonia from the combustion ash, it is extremely undesirable, especially if there are people working in the vicinity of the ash, because ammonia is considered a dangerous pollutant.

What is needed, therefore, is a method for eliminating or at least reducing the emission of ammonia from combustion ash, whether accumulated for disposal or used for other products, such as concrete.

Background Art

The use of combustion ash to form usable products has been taught by, for instance, Stockel, in U.S. 4,469,503, which describes the preparation of a fertilizer composition containing coal ash, as well as a water insoluble polymer which gradually decomposes to slowly

release nitrogen polymerized uniformly on the coal ash. In addition, Costopoulos and Newhouse teach the preparation of a concrete-like building material formed by combining fly ash with a bonding agent and air entrainer, water, and a foaming agent in U.S. 4,659,385. The preparation of protective and decorative coatings using pozzolonic fly ash in a hydraulic cement composition has been disclosed by Cornwell and Plunguian in U.S. 4,088,804.

10 Nitrogen oxides reducing processes which utilize ammonia, urea, or other nitrogenous compositions are still relatively new. Accordingly, the problem of ammonia emissions from combustion ash has only recently been appreciated. Consequently, little has been disclosed for
15 alleviating such undesirable emissions.

Epperly and Sprague, in U.S. 5,069,720, disclose a process for reducing the emission of ammonia from combustion ash when the ash is maintained in an accumulation such as in a strip mine or other unprotected environment.
20 The Epperly/Sprague method involves applying either a physical barrier composition or a chemical barrier composition, or both, to the combustion ash to prevent ammonia present therein from being emitted to the atmosphere. As is apparent, this method maintains the ammonia present in
25 the combustion ash and does not provide a means for eliminating the ammonia for further use of the ash, such as for the production of building materials.

European Patent 0135148 to Huller, Wirsching, and Hamm provides a discussion of the elimination of ammonia
30 or ammonium salts from combustion ash. This patent describes a process which involves mixing the ash from a coal power station, which has been treated with ammonia

in a catalytic nitrogen oxides reducing process, with calcium oxide (lime) or calcium oxidic materials along with surplus amounts of water. The ash is reacted with the lime for up to two hours in a reaction receptacle and a condensing device which condenses the ammonia liberated from the ash. Unfortunately, the process of this European patent involves the use of apparatus which can be expensive and is relatively time consuming. It can also reduce the pozzolonic properties of the ash. This can make the disclosed process undesirable, both in terms of economics and in terms of being able to adequately process all of the residue being produced in a boiler operating regularly.

Description of Invention

The present invention relates to a method for the removal of ammonia from combustion fly ash, which has become affixed as a by-product of post combustion flue gas treatment processes, especially processes for the reduction of nitrogen oxides present in the combustion effluent. The invention generally involves exposing the combustion fly ash to a stream of moving air under conditions effective to strip or liberate the affixed ammonia from the ash.

Fly ash is a particulate material collected from the effluent, or flue gases, of stationary combustion sources, such as coal, oil, or municipal solid waste (MSW) burning power plants. It generally comprises a very fine dust with particles mostly in the silt size range. The physical and chemical properties of fly ash vary according to the combustion source, depending on the source of fuel, burning and handling methods, and also the addition of materials both prior to and subsequent to combustion

(such as nitrogenous NOx reducing treatment agents), as well as the addition of materials to aid in the fly ash collection process.

The principle constituents of fly ash are silica (silicon dioxide, SiO_2), which is commonly present at a level between about 34% and about 55%, alumina (aluminum oxide, Al_2O_3), which is commonly present at a level of about 21% to about 30%, calcium oxide (CaO), which is commonly present at a level of about 5% to about 27%, and magnesium oxide (MgO), which is commonly present at a level of about 1.0% to about 5%. As is well known, the actual composition of fly ash can vary widely, and in fact, the ranges provided are merely representative of common fly ash compositions. In addition to those compositions detailed above, common combustion fly ashes also contain other components, as well as unburned carbon. The analyzed composition of several measured fly ashes from different sources is set out in Table I.

TABLE I*

	FLY ASH 1	FLY ASH 2	FLY ASH 3	FLY ASH 4	FLY ASH 5	FLY ASH 6	FLY ASH 7	FLY ASH 8
SiO ₂	48.7	47.0	34.0	49.0	35.0	39.0	43.0	55.0
Al ₂ O ₃	21.0	27.0	20.4	22.4	19.1	22.5	24.1	30.0
CaO	9.2	5.0	25.9	17.0	26.5	20.3	22.6	3.5
MgO	3.3	1.9	4.4	3.1	5.0	5.0	3.6	1.0
SO ₃	8.8	---	2.3	0.4	1.7	1.0	1.0	0.3
Fe ₂ O ₃	4.0	7.8	4.0	3.2	4.8	5.2	4.5	4.7
K ₂ O	2.0	3.2	0.2	0.1	0.1	0.2	---	---
TiO ₂	0.7	1.1	---	---	---	---	---	---
Na ₂ O	0.3	0.8	2.3	0.2	0.7	0.5	---	---
P ₂ O ₅	0.3	0.8	---	---	---	---	---	---
Moisture	---	---	0.0	0.3	0.0	0.1	0.0	0.0
Carbon	---	---	0.7	0.9	0.4	0.1	0.4	1.1

*All numbers are rounded to one decimal place and expressed as a percentage. Measurements not provided merely indicate measurements not taken. Table I does not reflect the entire composition of measured fly ashes, just specific components measured.

Generally, fly ashes have a specific gravity which can range between about 2.1 and about 2.6. Most of the particles of fly ash are glassy spheres, except for the carbon particles, which are somewhat larger and more angular than the inorganic particles. Fly ash particles generally have an average size which can range from less than about 1.0 to about 80 microns in diameter, more commonly between about 1.0 and about 20.0 microns in diameter.

The combustion ash is generated by the combustion of coal, oil, municipal solid waste, or other materials in a stationary combustion source such as an electricity generating utility or other like system. The ash is carried along with the combustion effluent, which often contains nitrogen oxides, a known pollutant. Nitrogen oxides are created when atomic oxygen and nitrogen are formed in the high temperature atmosphere generated in a stationary combustion source and chemically combine as nitrogen oxides. They are troublesome pollutants and comprise a major irritant in smog. In addition, NO_x can undergo a process referred to as photochemical smog formation and comprise a significant contributor to acid rain and have been implicated as contributing to the undesirable depletion of the ozone layer. Nitrogen oxides may also impact on the warming of the atmosphere commonly referred to as "the greenhouse effect".

The nitrogen oxides level in the combustion effluent can be reduced by the introduction of a nitrogenous treatment agent, either in and of itself or to facilitate a selective catalytic reduction process. The most common agents for the non-catalytic reduction of nitrogen oxides are urea and ammonia, which can be introduced according

to a number of different processes effective for reducing nitrogen oxides. Exemplary of these processes are those disclosed by Lyon, in U.S. 3,900,554, Arand, Muzio, and Sotter, in U.S. 4,208,386, and Arand, Muzio, and Teixeira, in U.S. 4,325,924, the disclosures of each of which are incorporated herein by reference.

In addition, the introduction of the nitrogenous treatment agent can be performed in a manner which is effective at reducing nitrogen oxides, but minimizes the amount of ammonia generated as ammonia slip or ammonia breakthrough. Such processes are taught by Epperly, Peter-Hoblyn, Shulof, Jr., and Sullivan, in U.S. 4,777,024; Epperly, Peter-Hoblyn, Shulof, Jr., Sullivan, Sprague, and O'Leary, in U.S. 5,057,293; Epperly, O'Leary, and Sullivan, in U.S. 4,780,289; and Epperly, Sullivan, Sprague, and O'Leary, in U.S. 5,017,347, the disclosures of each of which are incorporated herein by reference.

Recently, in a unique application of non-catalytic NOx reducing technologies, von Harpe, Pachaly, Lin, Diep, and Wegrzyn have taught a process for nitrogen oxides reduction which utilizes the hydrolysis products of urea, in International Application entitled "Nitrogen Oxides Reduction Using A Urea Hydrolysate", International Publication No. WO 92/02450, filed 1 August 1991, the disclosure of which is incorporated herein by reference.

The catalytic reduction of nitrogen oxides generally involves passing the effluent across the catalyst bed in the presence of ammonia. Selective catalytic reduction processes for reducing NOx are well known and utilize a variety of catalytic agents. For instance, in European Patent Application WO 210,392, Eichholtz and Weil disclose

cuss the catalytic removal of nitrogen oxides using activated charcoal or activated coke, with the addition of ammonia, as well as a catalyst. Kato et al., in U.S. 4,138,469, and Henke, in U.S. 4,393,031, disclose the catalytic reduction of NOx using platinum group metals and/or other metals such as titanium, copper, molybdenum, vanadium, tungsten, or oxides thereof with the addition of ammonia to achieve the desired catalytic reduction. Another catalytic reduction process is disclosed by Canadian Patent 1,100,292 to Knight, which relates to the use of platinum group metal, gold, and/or silver catalyst deposited on a refractory oxide. Mori et al., in U.S. 4,107,272, discuss the catalytic reduction of NOx using oxysulfur, sulfate, or sulfite compounds of vanadium, chromium, manganese, iron, copper, and nickel with the addition of ammonia gas. Additionally, the ammonia can be provided (at least in part) by the upstream introduction of urea under conditions designed to produce ammonia in the effluent to facilitate the catalytic reduction of NOx, as taught by Hofmann, Sun, and Luftglass in U.S. 4,978,514, and Luftglass, Hofmann, and Sun in U.S. 5,139,754, the disclosures of which are incorporated herein by reference.

Regardless of the specific method by which nitrogen oxides are being reduced by the introduction of a nitrogenous treatment agent, it is virtually impossible to prevent at least some ammonia slip. When this occurs, ammonia becomes affixed to the fly ash, primarily by being reacted therewith, and is absorbed thereinto. Most often, the ammonia is present in the ash in the form of ammonium salts, such as ammonium chloride, ammonium sulfate, and ammonium bisulfate, as well as absorbed free ammonia.

In order to prevent the fly ash from being emitted to the atmosphere, it is collected by conventional apparatus such as in a bag house, an electrostatic precipitator, or like means. The ash is then transported
5 either to disposal, such as in a landfill or strip mine, or to be reused such as for structural fill or in the formation of cement or other building materials.

In order to liberate or strip the affixed ammonia from the combustion fly ash after it has been collected
10 as described above, it is exposed to moving air under conditions effective to strip a substantial amount (i.e., at least about 40%) of the ammonia from the ash. Although this description is written in terms of moving air, the term will be understood to include dry air, as
15 well as air containing water vapor, and steam.

Preferably, the ash is exposed to the moving air under conditions effective to strip at least about 65% of the ammonia and most preferably at least about 90% of the ammonia therefrom. In order to most effectively strip a
20 substantial amount of the ammonia from the ash, the air should be at a temperature of at least about 300°F and preferably at least about 350°F. Although there is no true upper limit to the temperature of the air, there is no significant gain in efficiency if the temperature is
25 above about 650°F.

As noted, the air to which the ash is to be exposed should be moving. It is only necessary for the air to be moving at a rate sufficient to remove the ammonia from the vicinity of the ash in order to prevent reaffixation.
30 For this purpose, the flow rate of air should most preferably be capable of fluidizing the ash. This can occur at about five feet per minute per square foot of ash

across or through which the air is flowing. The rate of flow depends on ash depth, etc. Ammonia stripping will occur if the ash is fluidized or suspended in the air flow. The ash should be exposed to the flow of air for a
5 sufficient time to fluidize the ash, which depends on the temperature of the air -- the higher the temperature, the less exposure time required.

Desirably, the exposure should be for at least about one minute and preferably between about two and about ten
10 minutes in order to strip a significant amount of the ammonia from the ash.

The ash can be exposed to the flow of air while sitting in a collection apparatus or while being transported along a conveyor belt. In a preferred embodiment
15 of the invention, in order to maximize contact between the ash and the air stream, the flow of air is provided both across the surface of the ash and through the ash by bubbling the air through the ash from underneath. One apparatus in which this can be accomplished is referred
20 to as an "air slide" which is a conveyor which conveys the ash, by fluidizing it with low pressure air passing through a porous cloth. A slight incline in the conveyor causes the ash to be fed by gravity. The air is forced up through the cloth and through the ash in order to
25 strip the ammonia therefrom. After being exposed to the flow of hot air, the ash is then transported for disposal or reuse as described above.

The temperature of the moving air, and the time of exposure of the ash to the air are related, with long
30 times only necessary when the air is at low temperatures, and high air temperatures only necessary when short exposure times are required. For instance, when the ash is

stored in a silo, with long exposure times available, the air temperature need only be between about 300°F and about 400°F, although some ashes require higher temperatures (at least about 600°F), even when long exposure
5 times are available. However, when the ash is travelling on an air slide, and exposure times are limited to about one to about three minutes, the air temperature should be between about 450°F and about 650°F.

It is common to transport combustion fly ash by
10 forming a slurry of the ash in water or other liquid. Although this can facilitate transport, it is important that, when the ash is exposed to the flow of moving air, it be substantially dry -- that is, it has a moisture level of no greater than about 7%, advantageously no
15 greater than about 3%, more advantageously no greater than about 0.5% in order to effectively strip the ammonia from the ash.

Additionally, although the ash is normally alkaline (having a pH which usually varies between about 5.0 and
20 about 8.5), ammonia stripping can be aided by increasing the alkalinity (i.e., raising the pH) of the ash. The increased alkalinity will cause evolution of ammonia, allowing it to be carried away by the moving air. An increase in the alkalinity can be accomplished by adding
25 to the ash an alkaline agent, such as lime, in amounts sufficient to raise the ash alkalinity to any measurable extent. Increasing the ash alkalinity may be undesirable, however, depending on the end use of the ash. For instance, highly alkaline ash may not be suitable for use
30 in certain building materials.

The air, now laden with ammonia, can be treated to remove the ammonia therefrom by conventional means. Alternatively, the hot air can be recycled as combustion air to recover the heat, and burn the ammonia.

- 5 The use of the present invention to achieve substantial reductions in the amount of ammonia affixed to post-combustion fly ash is illustrated by reference to the following example.

Example

- 10 A pilot stripping unit having a regulated hot air supply duct constructed of 4" carbon steel pipe approximately 5' long is provided. Along the length of the supply duct a 1" slip stream tap and 2 thermowells are installed to monitor the supply air temperature and educt
15 contaminated ash into the hot air stream. The hot air source is a self contained 30,000 British Thermal Unit (btu) space heater. Downstream and inline of the flow path of the supply duct, a collection chamber with filter bags is used to collect the processed ash. Downstream of
20 the collection chamber is a flow control damper and exit air thermometer.

- A combustion fly ash (500 grams) having an ammonia concentration of 272 parts per million (ppm) is educted into a hot air stream in the pilot stripping unit at a
25 variety of temperatures for two minutes and then collected in filters and the final ammonia concentration measured. The results are set out in Table III.

TABLE III

	TEMPERATURE (°F)	TIME (min.)	BASELINE NH ₃ (ppm)	FINAL NH ₃ (ppm)	% REDUCTION
5	450	2	272	5	98.2
	450	2	272	0	100.0
	300	2	272	0	100.0

A review of this example makes it clear that practice according to the process of the present invention will effectively strip a substantial amount of ammonia affixed to combustion fly ash.

The above description is for the purpose of teaching the person of ordinary skill in the art how to practice the present invention, and it is not intended to detail all of those obvious modifications and variations of it which will become apparent to the skilled worker upon reading the description. It is intended, however, that all such obvious modifications and variations be included within the scope of the present invention, which is defined by the following claims.

What is Claimed is:

1. A process for reducing the amount of ammonia affixed to a combustion fly ash, comprising combusting a fuel under conditions effective to form a combustion fly ash and collecting said ash; and exposing said ash to a flow
5 of air which is at a temperature of at least about 300°F for at least about one minute.
2. The process of claim 1, wherein said air is at a temperature of at least about 350°F.
3. The process of claim 2, wherein said air is at a temperature of no greater than about 650°F.
4. The process of claim 1, wherein said ash is exposed to said flow of air for at least about two minutes.
5. The process of claim 4, wherein said air is flowing at a rate sufficient to effectively fluidize the ash.
6. The process of claim 1, wherein said ash has a moisture level no greater than about 7%.
7. The process of claim 1, wherein said fuel comprises coal, oil, or municipal solid waste.
8. The process of claim 1, wherein the pH of said ash is raised by the addition of an alkaline agent.
9. The process of claim 1, wherein said air comprises steam.
10. A process for reducing the amount of ammonia affixed to a combustion fly ash comprising:

i. combusting a fuel under conditions effective to form a combustion effluent containing a fly ash and nitrogen oxides;
5

ii. treating said effluent to reduce the nitrogen oxides concentration therein by introducing a nitrogenous treatment agent into the effluent under conditions effective to cause affixation of ammonia to said fly ash;

10 iii. collecting said fly ash; and

iv. exposing said fly ash to a flow of air which at a temperature of at least about 300°F for at least about one minute, wherein said flow of air strips away the ammonia contained in said fly ash.

11. The process of claim 10, wherein said fuel comprises coal, oil, or municipal solid waste.

12. The process of claim 10, wherein said nitrogenous treatment agent comprises urea, ammonia, the hydrolysis products of urea, or mixtures thereof.

13. The process of claim 10, wherein said air is at a temperature of at least about 350°F.

14. The process of claim 13, wherein said air is at a temperature of no greater than about 650°F.

15. The process of claim 10, wherein said ash is exposed to said flow of air for at least about two minutes.

16. The process of claim 15, wherein said air is flowing at a rate sufficient to effectively fluidize the ash.

17. The process of claim 10, wherein said ash has a moisture level no greater than about 7%.

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18. Th process of claim 10, wher in th pH of said ash is raised by the addition of an alkaline agent.

19. The process of claim 10, wherein said air comprises steam.

INTERNATIONAL SEARCH REPORT

 International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C01B 21/00, 21/20

US CL : 588/244; 423/235,237,238, DIG. 16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 588/244; 423/235,237,238, DIG. 16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,911,900 (Horch et al.) 27 March 1990, see col. 1 lines 43-53; col. 3 lines 32-61 and col. 4 lines 6-17.	1-7, and, 9-18
Y	US, A, 4,572,703 (Hino et al.) 25 February 1986, see col. 1 lines 59-60.	9 and 19
A	US, A, 4,325,924 (Arand et al.) 20 April 1982, see col. 1 lines 48-62 and col. 4 lines 9-17.	7 and 10-18
A	US, A, 2,606,863 (Rehbein) 12 August 1952, see col. 2 lines 16-37.	1 and 10
A,P	US, A, 5,211,926 (Martin et al.) 18 May 1993, see col. 2 lines 14-62.	1,9,10 and 19



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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